Sintering Behavior of Diboride Based Materials

Matt Gasch, Michael Gusman

ELORET Inc

Edward Irby, Don Ellerby, Sarah Beckman and Sylvia Johnson

NASA Ames Research Center

ELORET

Thermal Protection Materials and Systems Branch

Contributors

Ames Research Center

Dr. Munir, UC Davis

CERAC™ incorporated

Mark Drezdzon, Manager of New Product and Process Development

ELORET

Objective

Ames Research Center

- Brief History of Diboride Research
- Processing Overview
- Sintering Studies
- Conclusion

ELORET

Development of Ultra High Temperature Ceramics

Ames Research Center

- UHTCs are a family of ceramic materials, including diborides of Hf and Zr, with extremely high melting temperatures
- Previous studies have indicated good oxidation resistance in simulated reentry environments
  - ManLabs 1960's and 1970's
  - ARC 1990's
    - Ground based research: initial materials development by external vendors, Arc Jet testing, computer modeling, etc.
    - SHARP-B1(1997) and SHARP-B2 (2000) ballistic flight experiments
      - » Materials provided by external vendors
      - » Different vendors used for each flight experiment
      - » Focus on flight experiment not on materials development
  - Detailed studies still required to define use environments (Single and Multi-Use Temperatures)

ELORET

HfB_2-SiC

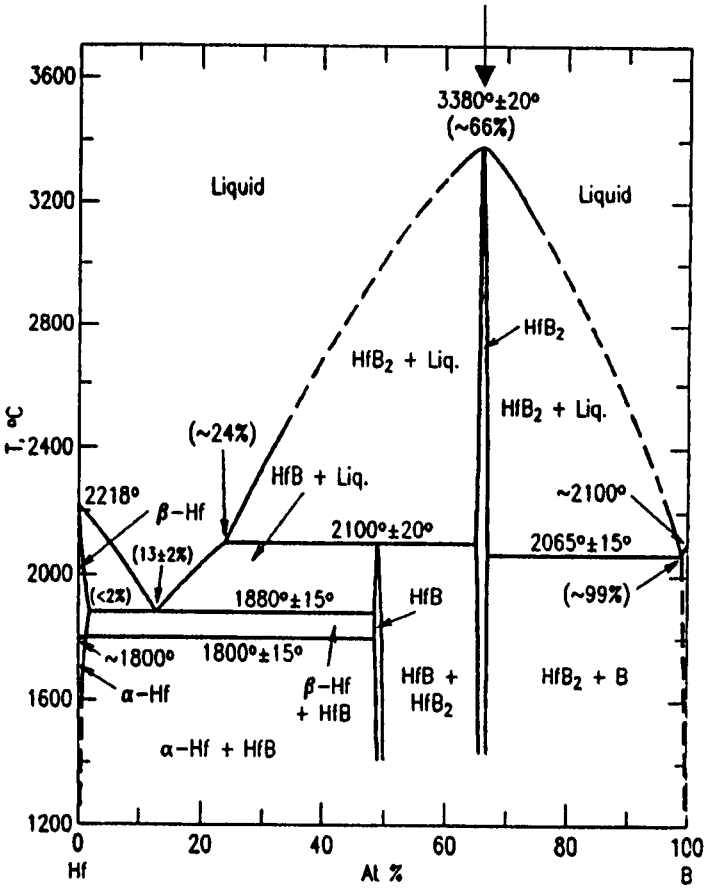
Ames Research Center

HfB_2

- HfB_2 has a narrow range of stoichiometry with a melting temperature of 3380°C
- Density = 11.2 g/cc

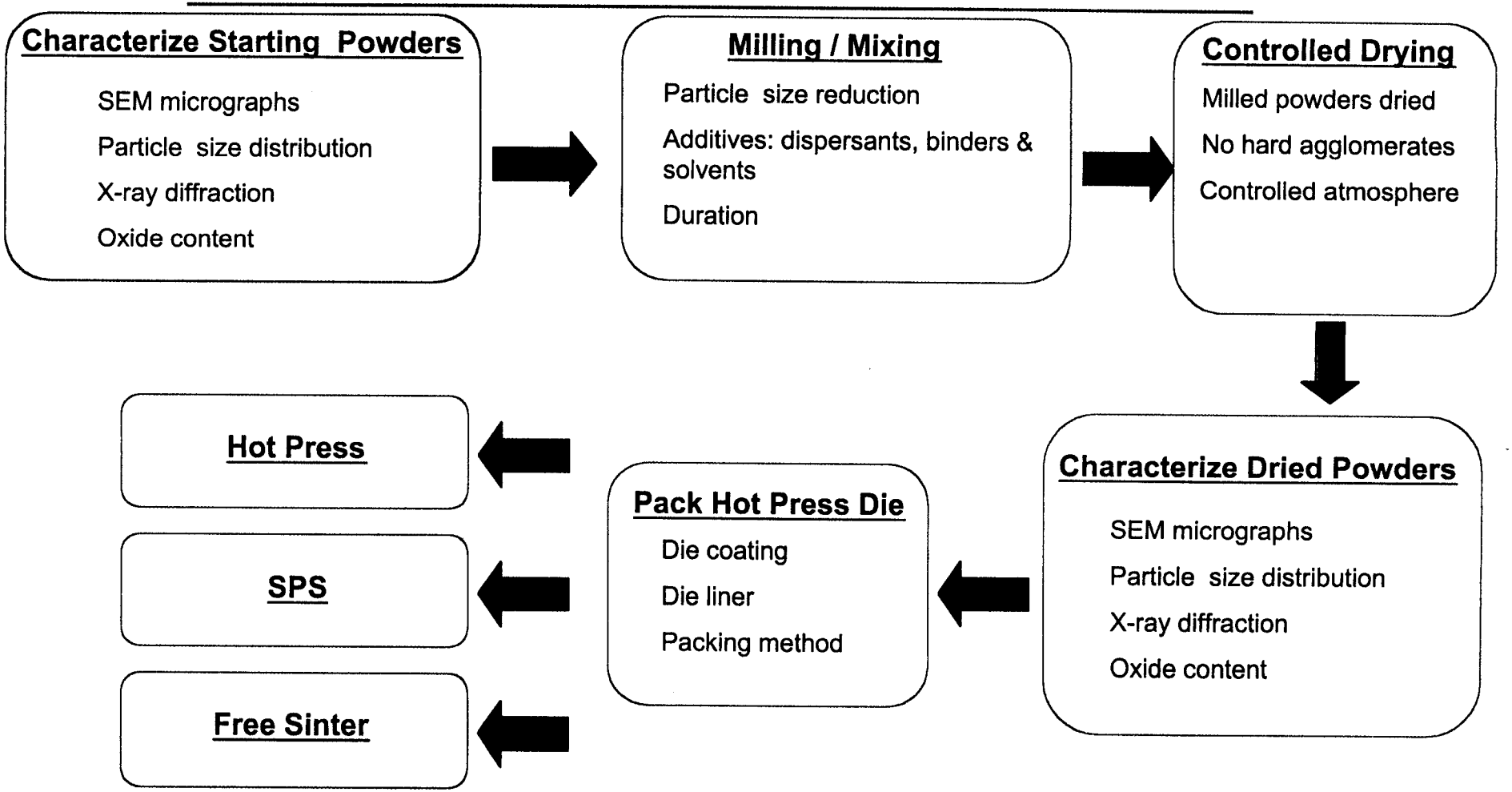
SiC

- aids densification
- limits grain growth
- may enhance oxidation resistance
- Density = 3.2 g/cc



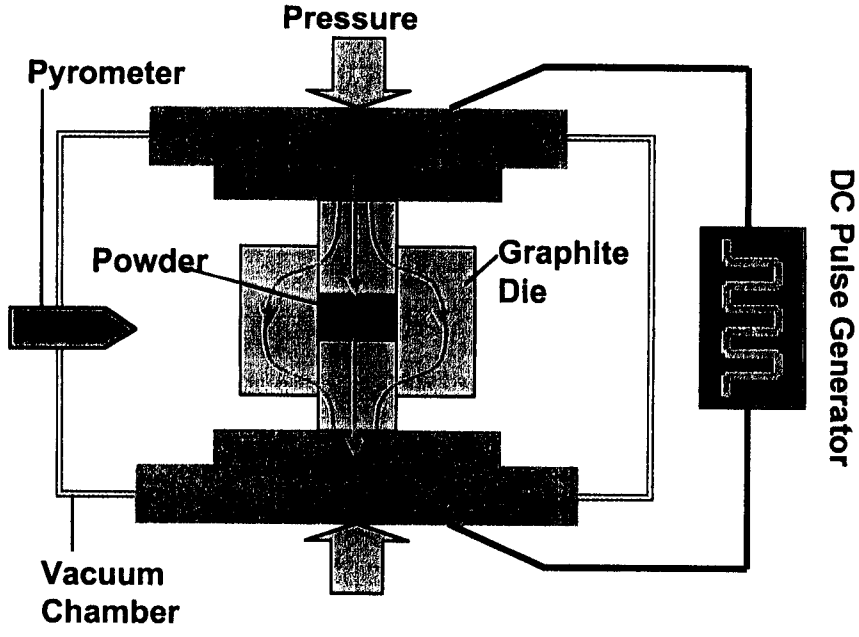
ELORET

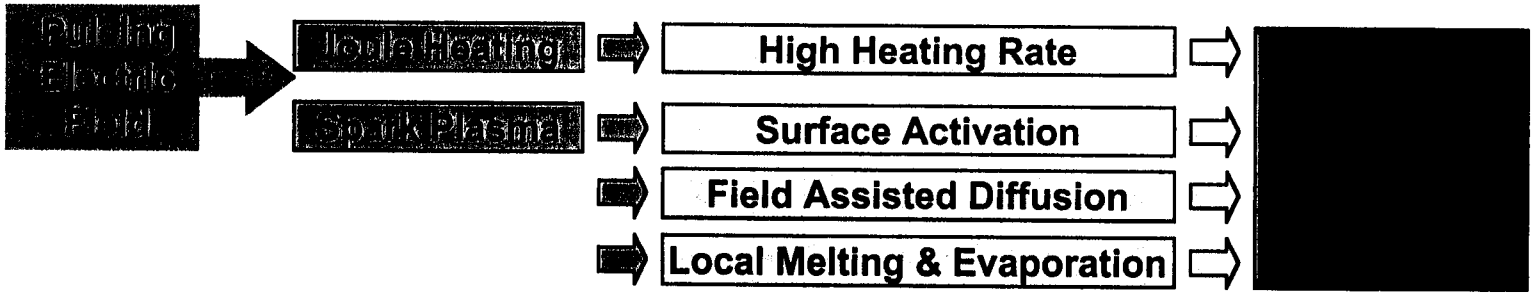
General Processing Route



ELORET

Spark Plasma Set-up





ELORET

Introduction Cont.

Ames Research Center

- Spark Plasma Sintering (SPS) is a novel processing technique useful in consolidating difficult materials
- Ultra fast consolidation allows microstructures not obtainable by conventional hot-pressing

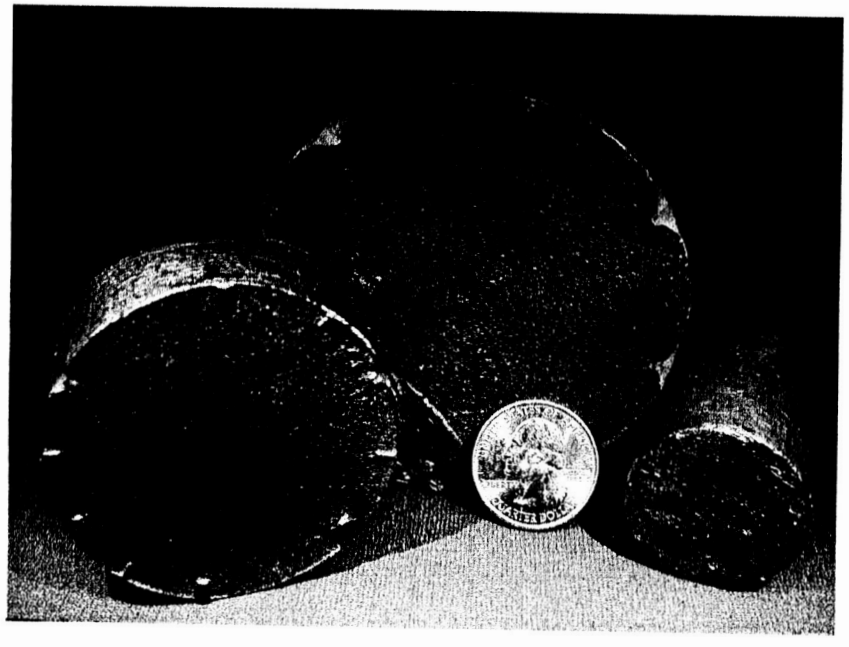
Omori, M., "Sintering, Consolidation, Reaction and Crystal Growth by the Spark Plasma System (SPS)", Mat. Sci. Eng. A, **[A287]** 183-188 (2000).

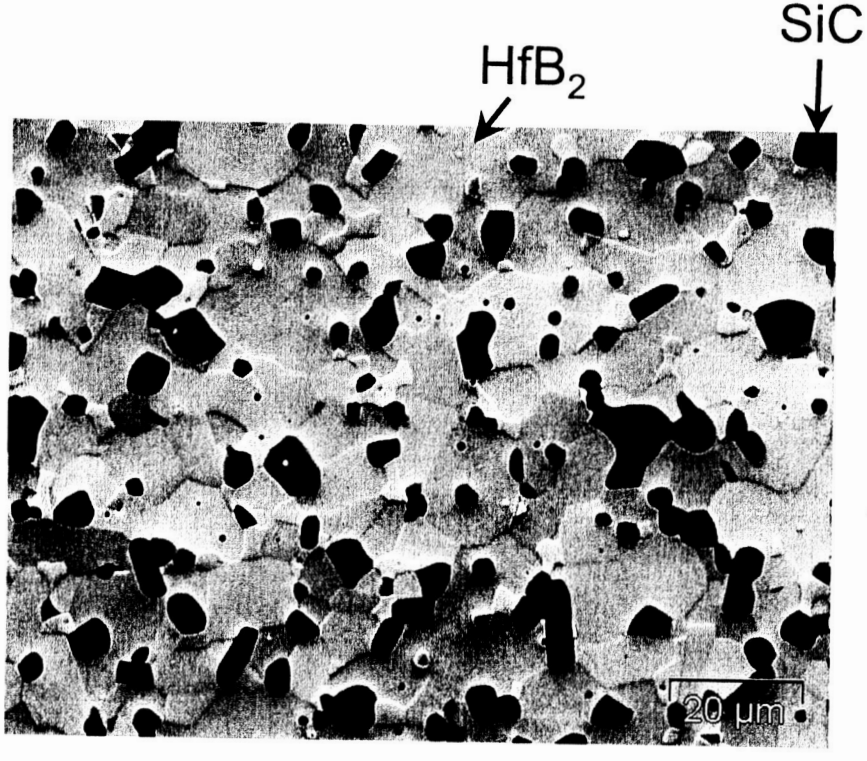
ELORET

Ames Family of HfB_2-SiC Ceramics

Ames Research Center

Current processing techniques are capable of realizing 1" (25mm), 2" (50mm) and 3" (75mm) diameter billets





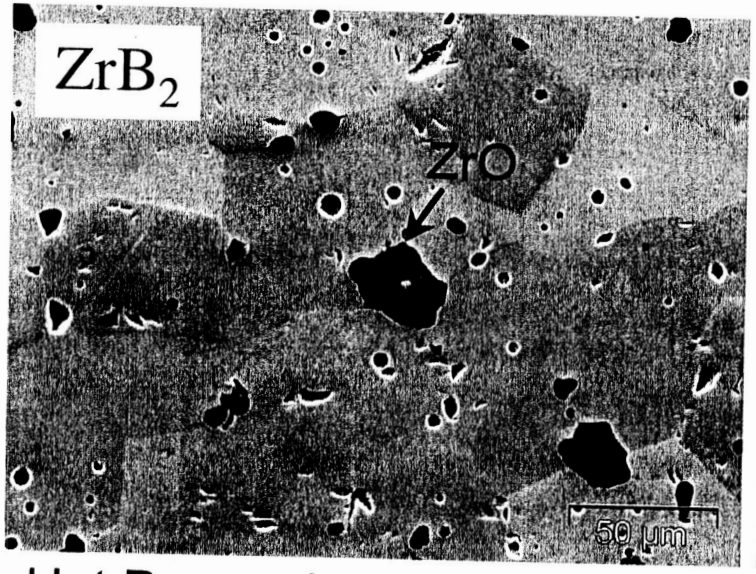
Hot pressing HfB_2 with SiC yields fully dense materials

ELORET

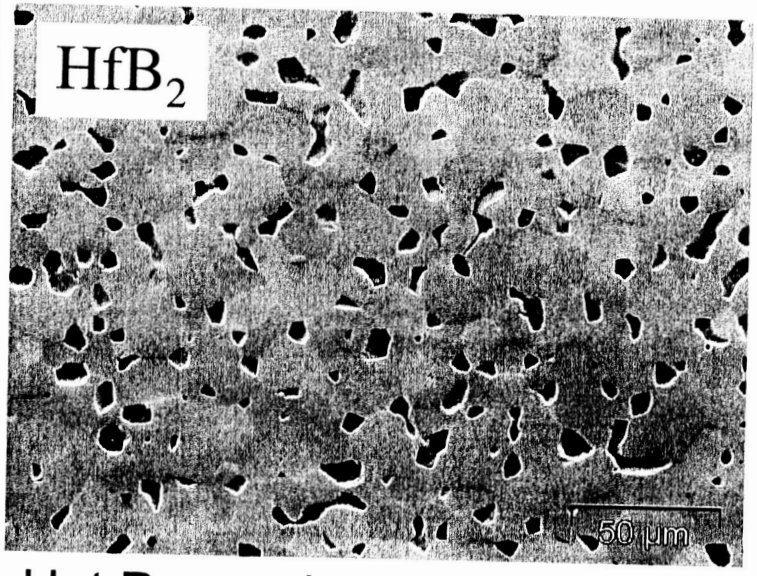
Hot Pressed - Pure Diborides

Ames Research Center

- Raw powders sinter poorly with extensive porosity when sintered at the same conditions as those materials sintered with SiC (2000-2200°C)



Hot Pressed
2000°C - 1 hour



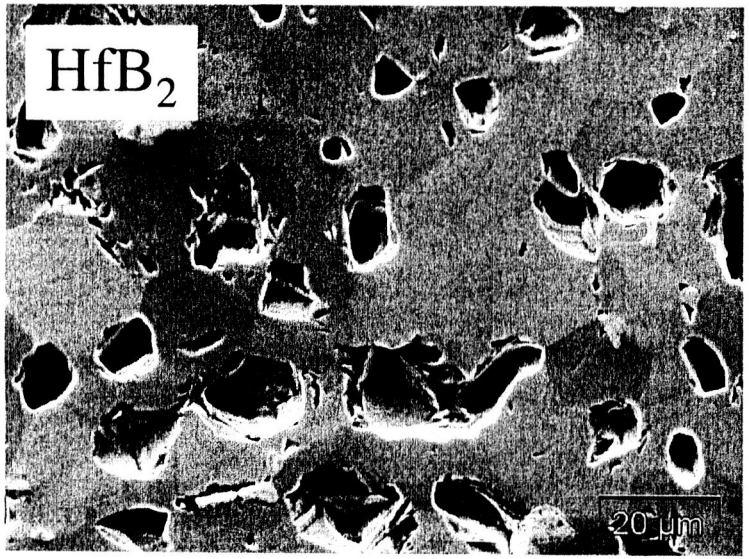
Hot Pressed
2200°C - 1 hour

ELORET

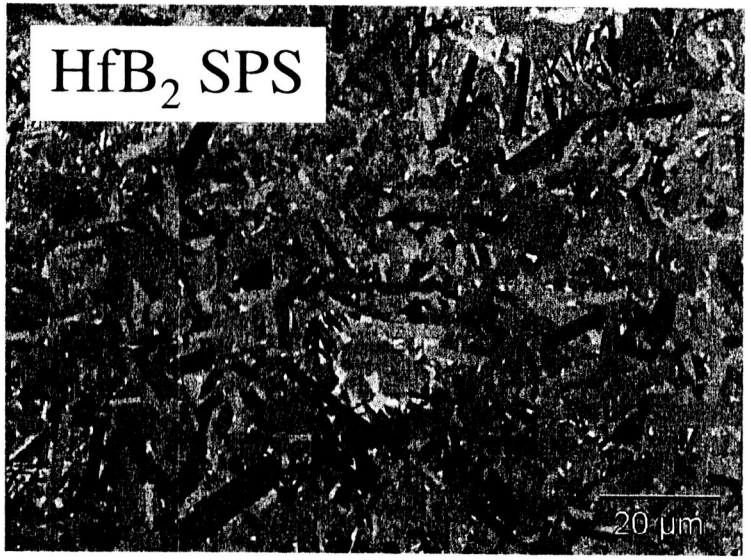
Alternatively Processed Pure HfB_2

Ames Research Center

- Hot pressed materials were porous
- SPS materials sintered with minimal porosity, reduced grain size



Hot Pressed
2200°C - 1 hour



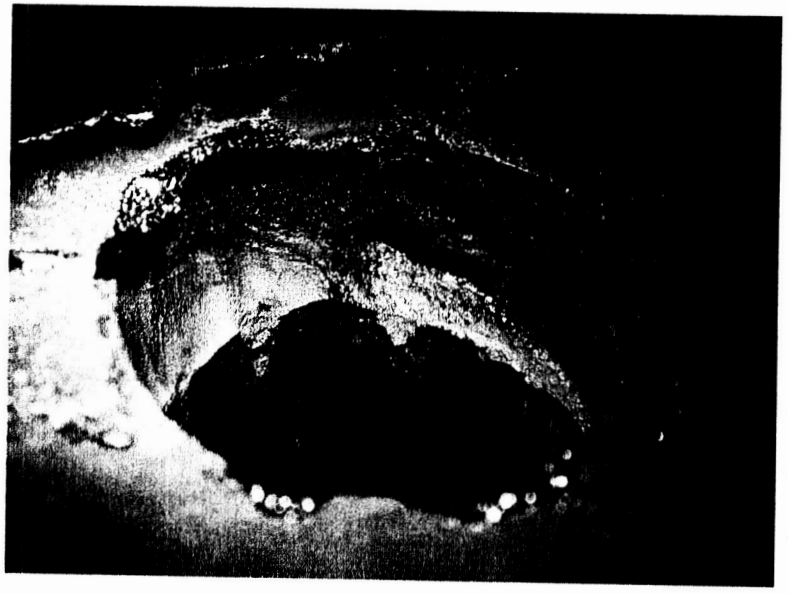
Spark Plasma Sintered
1900°C - 10 minutes

ELORET

Hot Pressed - Pure Diborides

Ames Research Center

- Attempts to remove porosity by hot pressing HfB_2 and ZrB_2 at a higher temperature failed when raw powders became molten and leaked from the die.

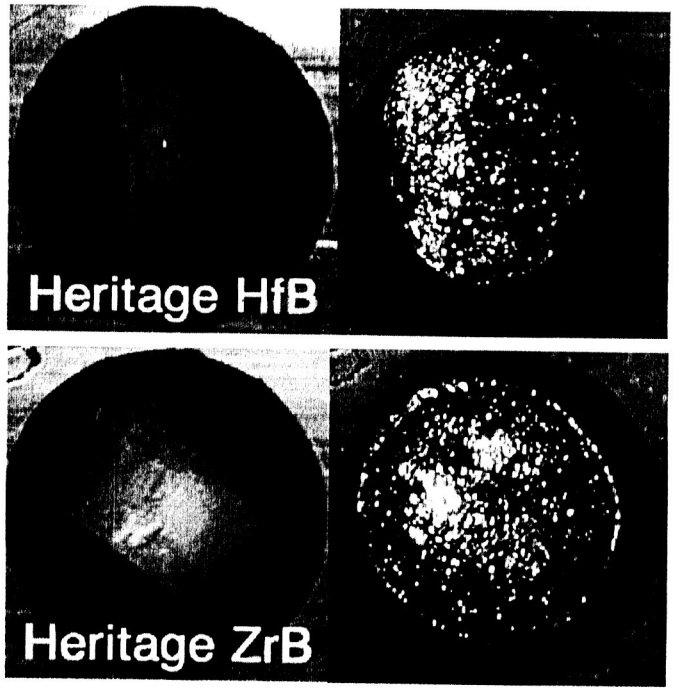


ELORET

Free Sintered Diborides

Ames Research Center

- To remove the effects of pressure, pellets were pressed from raw powders and placed in graphite crucibles
- After furnace exposure of only 30 minutes pure HfB_2 and ZrB_2 powders were seen to have melted



Free Sintered
2350°C - 30 minutes

ELORET

Raw Material Processing

Ames Research Center

MOxide + B + Boron Carbide + C ⇨ MBoride + Side Products

- Typical Metal Boride reaction used is capable of yielding large quantities of powder but can contain side products (borates) or a product with off target stoichiometry

M + B ⇨ MBoride

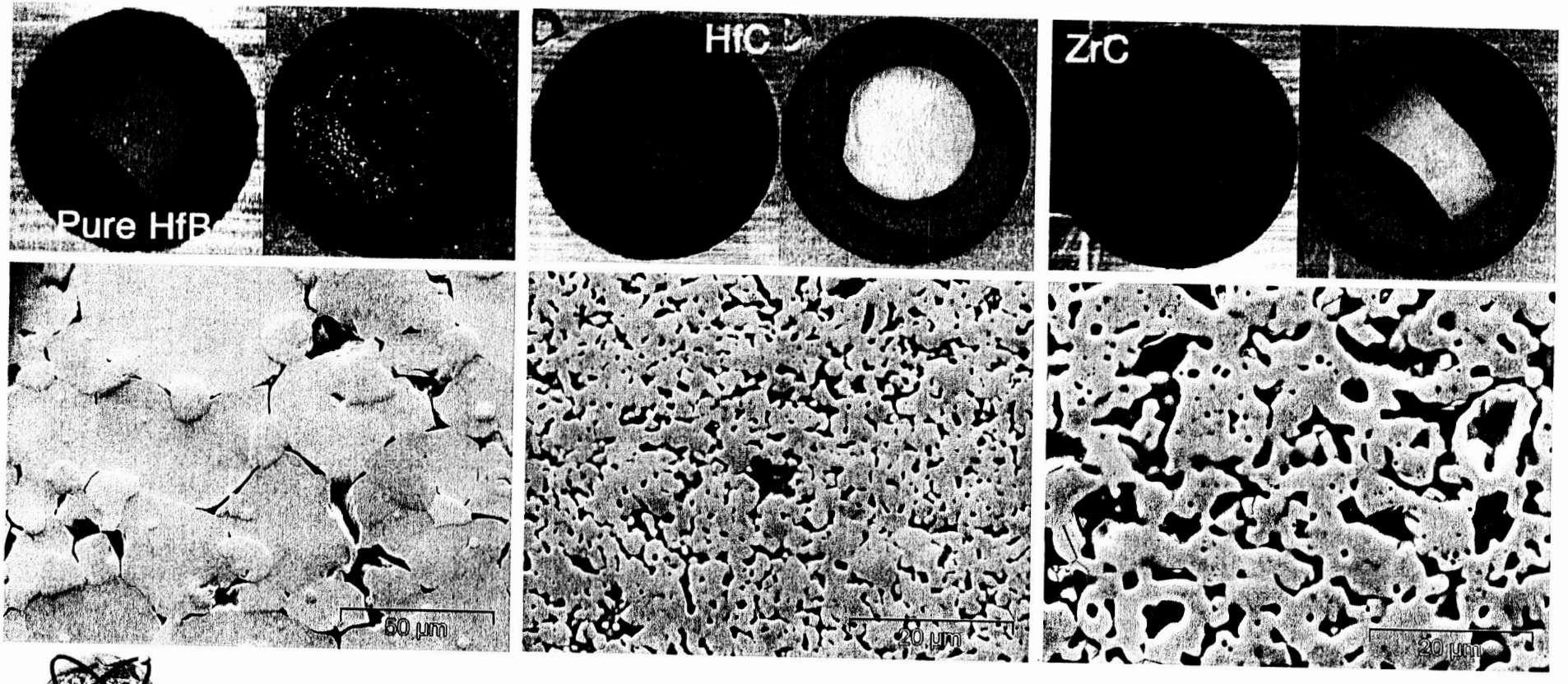
- Elemental reaction (under investigation) can yield a more stoichiometric product free from most side products
- Currently yields small quantities of powder but scalability is under investigation by our vendor, Cerac, Inc.

ELORET

Other Free Sintered Borides and Carbides

Ames Research Center

- HfB_2 formed from an elemental reaction did not melt, neither did the carbides of Hf and Zr



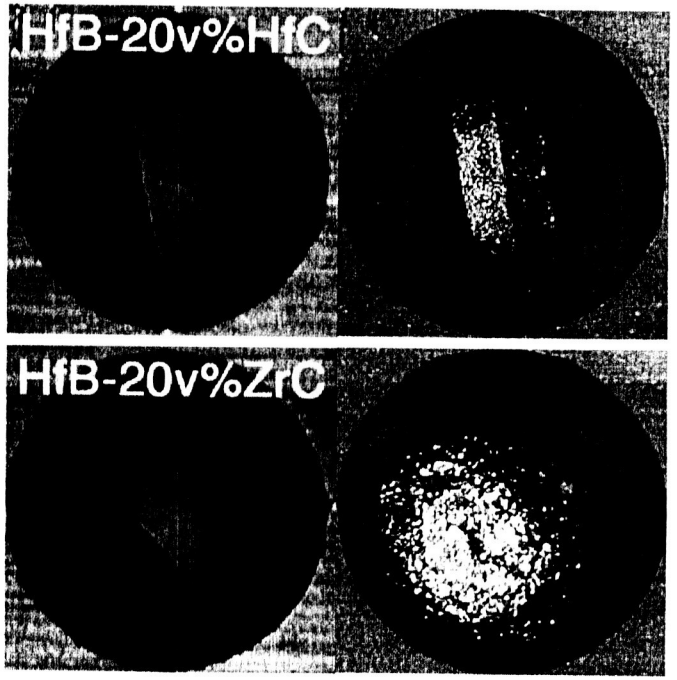
All samples Free Sintered @ 2350°C - 30 minutes

ELORET

Boride / Carbide Mixtures

Ames Research Center

- Free Sintered Boride/Carbide mixtures show varied results, still under investigation



Free Sintered
2350°C - 30 minutes

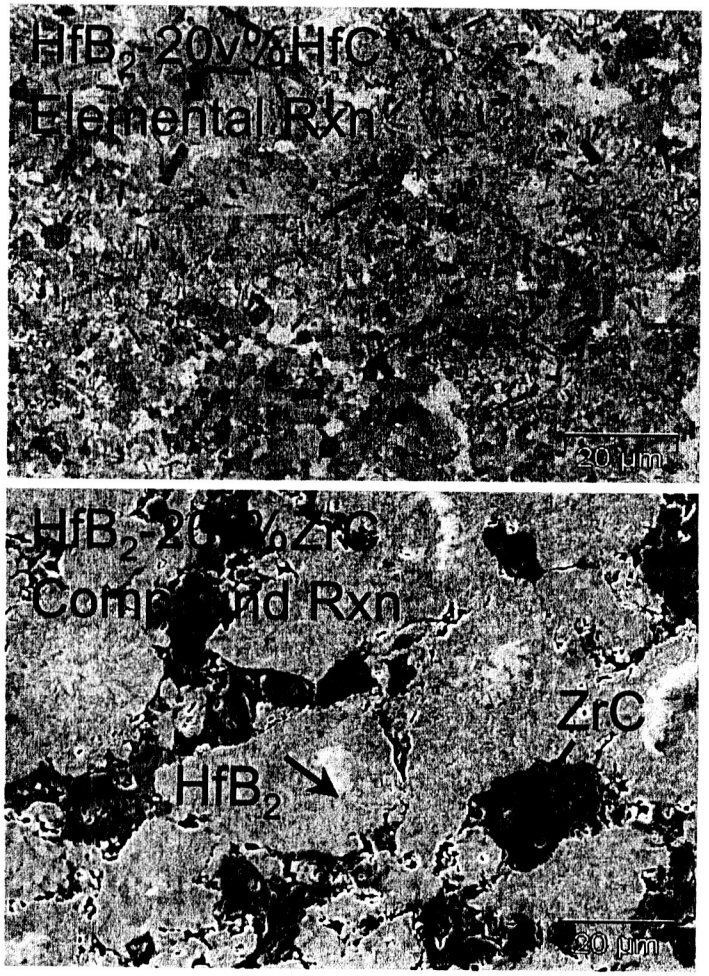
ELORET

Alternatively Processed Boride / Carbide Mixtures

Ames Research Center

- Elemental reaction of Hf-B-C sinters to near full density yielding a microstructure with a even distribution of fine grains

- Compound reaction of Hf-B & ZrC does not sinter well, yielding phase separation and a porous microstructure



Spark Plasma Sintered
1900°C - 10 minutes

ELORET

Conclusions

Ames Research Center

- Refractory hafnium and zirconium borides and carbides are being investigated for their high temperature properties
- Raw materials do not hot press well but can be consolidated with alternate methods.
- Increased hot press temperatures revealed that as received hafnium and zirconium diboride were found to liquefy well below their theorized melting point.
- Improvements in raw material processing and powder mixing show promising results

ELORET